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Enantiomerically Pure Palladacycles with one Stereogenic Csp^3 Center Directly Bonded to the Metal

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Abstract: The reaction of homochiral 1-methyl (ethyl and phenyl)-2-*p*-tolylsulfinyl ethanones with $Pd(OAc)_2$/AcOH yield enantiomerically pure trimer orthopalladated compounds containing a stereogenic carbon C-sp^3 directly joined to the Pd atom.

In general, the studies related to the use of the sulfoxides as coordinating species with different transition metals[1] has been related to the two possible coordination sites (sulfur and oxygen) present in their structures. The DMSO complexes are the most widely known.[2] In most of the Pd(II) and Pt(II) complexes, the association takes place through the sulfur atom, which has been considered to be a consequence of the electronic and steric factors, which lead to stronger S-metal bond with respect to the O-metal bonds.[3,4] This tendency of the sulfinyl sulfur to coordinate metals such as palladium is also reflected in the fact that the only known orthopalladiated compounds derived from benzylsulfoxides use the sulfur lone electron pair to precoordinate to the metal.[5] Carbon-carbon coupling reactions involving palladium complexes are commonly encountered for most known methods of C-C bond formation. Nevertheless, these reactions are generally restricted to sp^2 type centers, mainly due to the β–elimination process of the adjacent hydrogens,[6] thus, disregarding the coupling of stereogenic carbons. Therefore, the use of the sulfoxides as homochiral ligands is rare, and most examples are related to the use of methyl *p*-tolylsulfoxide as ligand.[4] In these complexes, usually the metals are bonded to the sulfur atom of the sulfinyl group. With this in mind, it would be interesting to prepare compounds with the sp^3 hybridized stereogenic C-atom directly bonded to the palladium atom.

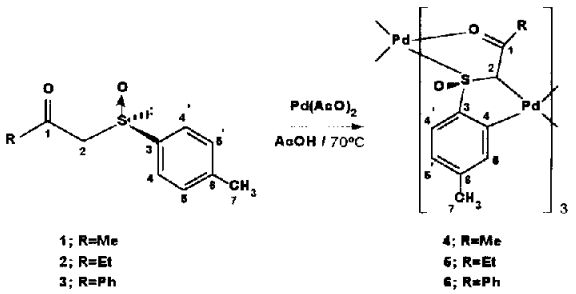
Orthopalladated compounds are known stable compounds exhibiting a C-Pd bond. These compounds have been widely studied due to their interest in structural and synthetic aspects. Nevertheless, orthopalladated complexes derived from arylsulfoxides, which involve the precoordination of the sulfinyl oxygen to the metal, have never been reported.

Our current interest in the orthometallation processes,[7,8] as well as the use of the enantiomerically pure β–ketosulfoxides in asymmetric synthesis,[9] prompted us to investigate the behavior of these substrates (R-CO-CH_2-SO-*p*-Tol) with metals like Pd. The interest of these studies was inherent to the structure of the ligands,

which contain several coordination sites (carbonyl and sulfinyl oxygen) and one stereogenic center (sulfinyl sulfur). This steregenic center, easily available in high enantiomeric purity, could be transferred to the complexes derived from them. In addition, β–ketosulfoxides offer the possibility to form orthometallated species involving the precoordination O-Metal, or palladacycles resulting from the initial insertion of the electrophilic Pd(II) salts into the strongly acidic H-C bonds flanked by the SO and CO groups,[10] followed by the orthometallation of the *p*-tolyl ring. In a previous communication[11] we have reported the synthesis and structural characterization of the complex obtained from $Pd(OAc)_2$ and (***R***)-3-*p*-tolylsulfinyl propanone 1, mainly based on the X-ray diffraction studies. In this paper we have extended the reaction to other β-ketosulfoxides, which demonstrates that it is a general method to synthetize the complexes. Additionally we report the spectroscopical data which allow the structural assignment of the complexes and suggest the stereochemical course to explain the high stereoselectivity of thus reactions.

Results and discussion

The reactions between $Pd(OAc)_2$ and (***R***)-3-*p*-tolylsulfinyl propanone **1**, (***R***)-1-*p*-tolylsulfinyl-2-butanone **2** or (***R***)-1-phenyl, 3-*p*-tolylsulfinyl propanone **3** in acetic acid at 70°C under nitrogen for 48-72 hours afforded the complexes **4-6** respectively, after chromatographic purification.



Scheme 1

The microanalytical data for **4**, **5** and **6** (see Experimental Section) are consistent with the empirical formulas $C_{10}H_{10}O_2SPd$, $C_{11}H_{12}O_2SPd$ and $C_{15}H_{12}O_2SPd$, which indicates the structure $[LPd]_n$. The absence of the bridging acetates was confirmed from the lack in the IR spectra of the two bands (1580 and 1420 cm^{-1}).[12] The C=O stretching frequencies appear 139-153 cm^{-1} lower in complexes **4**, **5** and **6** (1556, 1570 and 1522 cm^{-1}) than in their corresponding ligands **1**, **2** and **3** (1711, 1709 and 1675 cm^{-1}), which suggests that the carbonyl oxygen must be involved in the coordination (the coordination of the C=O to palladium usually

results in a slight shift of the C=O stretching mode to lower frequencies). The high value of the observed $\Delta\nu$ is similar to that observed for the carbonyl group associated to palladium in the complex **7** (fig. 1).[13] This large effect could be a consequence of the double association of the fragment O=C-CH_2- with two metal atoms. In this case, it suggests a similar behavior for our ligands **1, 2** and **3**, which would became doubly associated to two palladium atoms. The absence of any strong IR bands for the complexes **4, 5** and **6** in the region 830-1030 cm^{-1} is consistent with sulfur coordination in these complexes.[14] Coordination of the sulfoxide ligand via oxygen or sulfur is known to affect a decrease or increase respectively in the S=O stretching frequency.[14] The S=O stretch is tentatively assigned to the strong band 1114 cm^{-1} for **4**, 1127 cm^{-1} for **5** and 1116 cm^{-1} for **6**, which suggests coordination via sulfur. Compound **7**[13] exhibits this absorption at 1134 cm^{-1}. Finally, the IR spectra of compounds **4, 5** and **6** show one weak band at 544-580 cm^{-1} and a further stretch at 450 (compound **4**, **5**), or 493 cm^{-1} (compound **6**), which were tentatively assigned to Pd-C and Pd-S bonds respectively.

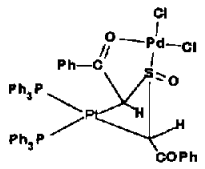


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Figure 1

Table 1. ^{1}H NMR data (ppm) for ligands **1, 2** and **3** and their palladium complexes **4, 5** and **6**[a]. See Scheme 1 for numbering.

Proton	Ligand **1**	Complex **4**	Ligand **2**	Complex **5**	Ligand **3**	Complex **6**
H2	3.83, m, 2H[b]	5.26, s, 1H	3.8, m, 2H[b]	5.28, s, 1H	4.43, m, 2H[b]	5.91, s, 1H
H4	7.53, m, 1H[c]	---	7.55, m, 1H[c]	---	7.59, m, 1H[c]	---
H4'	7.53, m, 1H[c]	7.08, d (7.9), 1H	7.55, m, 1H[c]	7.09, dd (7.8, 0), 1H	7.59, m, 1H[c]	7.1, d (7.9), 1H
H5	7.27, m, 1H[c]	7.16, s, 1H	7.35, m, 1H[c]	7.16, dd(1.3, 0), 1H	7.35, m, 1H[c]	7.17, d (0.81), 1H
H5'	7.27, m, 1H[c]	6.79, d (7.9), 1H	7.35, m, 1H[c]	6.79, dd(7.8, 1.3), 1H	7.35, m, 1H[c]	6.78, dd (7.9, 0.81), 1H
H7	2.39, s, 3H	2.17, s, 3H	2.42, s, 3H	2.19, s, 3H	2.40, s, 3H	2.26, s, 3H
R=CH_3	2.21, s, 3H	2.48, s, 3H				
R=Et			1.02, t(7.3), 3H	1.24, t(7.2), 3H		
			2.52, dc(7.3, 3.8), 2H	2.85, ABX_3, 2H		
R=Ph					7.40-7.90, m, 5H	7.20-7.60, m, 5H

[a] The numbers in parentheses correspond to $J(^1H\text{-}^1H)$ in Hz. s = singlet, t = triplet, dd = double doblet, dc = double quartet, m = multiplet;. [b] AB system. [c] These four protons form an AA'BB' system.

The ^{1}H NMR data for compounds **1, 2** and **3** with their corresponding palladium complexes are depicted in Table 1. One of the aromatic protons of the *p*-tolyl group is absent in all three complexes, reflected in the pattern exhibited by the remaining three protons, indicating orthopalladation has taken place on the ring joined to the sulfur. Besides, the signal corresponding to the methylene group flanked by the S=O and C=O groups (H2 in Table 1) in the ligands appears, in the complexes **4-6**, strongly deshielded ($\Delta\delta$ = 1.43-1.48 ppm). This signal integrates by one proton, which suggests the formation of one Pd-C bond and thus, a five membered

palladacycle involving C-2 and C-4. Shielding observed for the protons of the orthometallated ring could be due to the flow of charge from the electron-rich (d^8) metal atom into the aromatic ring (π-back bonding).[15]

The ^{13}C NMR data of the ligands **1-3** and those of their palladium complexes **4-6** are shown in Table 2. Spectra were assigned by heteronuclear 2D correlation spectroscopy[16] and quaternary carbon atoms by the heteronuclear NOE.[17] The comparison between the spectra of the ligands and complexes reveals that the main differences are observed in the signals corresponding to the carbons C1-C4 which are directly involved in the cyclopalladation. When a Pd-C aliphatic bond is formed, a small deshielding effect ($\Delta\delta$ ~ 5 ppm)[18] has been reported, which became larger in the case of a Pd-C aromatic bond ($\Delta\delta$ ~ 18 ppm),[18] probably due to the Pd-C back-bonding. In the case of complexes **4-6**, the effect is higher for the aliphatic carbons ($\Delta\delta$ (C2) ~ 13-15 ppm) and lower for the aromatic carbons ($\Delta\delta$ (C4) ~ 12 ppm). The orthometallation also determines the deshielding of the ortho positions with respect to that bonded to palladium, which is higher for the carbon remaining to the cyclopalladated ring.[8] This is also the case of C3 ($\Delta\delta$ ~ 9 ppm) and C5 ($\Delta\delta$ ~ 6 ppm) in these complexes. This effect could be responsible for the high chemical shift observed for C2 (directly bonded to palladium and adjacent to the sulfur atom, also bonded to the metal). The lower $\Delta\delta$ observed for C4 could be a consequence of the decrease of the palladium ability to back-bond due to the Pd-S interaction. Finally, the strong deshielding observed for C1 are consistent with the association Pd-O–C deduced from the IR data.

Table 2. ^{13}C NMR parameters (δ, ppm) of the ligands **1-3** and those of the complexes **4-6** in $CDCl_3$. See Scheme 1 for numbering.

	Complex **4**	Ligand **1**	$\Delta\delta$ (4-1)	Complex **5**	Ligand **2**	$\Delta\delta$(5-2)	Complex **6**	Ligand **3**	$\Delta\delta$ (6-3)
C-1	214.9	199.3	15.6	218.7	204.3	14.4	204.7	191.3	13.4
C-2	85.4	68.2	17.2	83.8	67.7	16.1	81.6	65.9	15.7
C-3	148.1	139.2	8.9	148.3	139.5	8.8	148.4	139.8	8.6
C-4	135.5	123.6	11.9	135.1	123.0	12.1	135.8	124.1	11.7
C-4'	127.1	123.6	3.5	127.1	123.0	4.1	127.0	124.1	2.9
C-5	135.0	129.8	5.2	135.6	129.0	6.6	135.8	129.8	6.0
C-5'	126.4	129.8	-3.4	126.4	129.0	-2.6	126.4	129.8	-3.4
C-6	141.9	141.7	0.2	141.8	141.9	-0.1	141.8	141.9	-0.1
C-7	21.5	21.1	0.4	21.5	21.2	0.3	21.5	21.3	0.2
R=CH_3	28.1	31.6	-3.5						
R=Et				34.0	38.1	-4.1			
				8.4	6.9	1.5			
R=Ph									
C_{ipso}							134.4	135.8	-1..4
C_{ortho}							130.0	128.6	1.4
C_{meta}							128.3	128.6	-0.3
C_{para}							134.3	133.9	0.4

The spectroscopic data suggests the structure depicted in Scheme 1 for complexes **4-6**. The high solubility of the complexes suggested a non polymeric structure, while their mass spectra showed ions with m/z = 901.6 (for **4**), 943.8 (for **5**) and 1088.0 (for **6**), suggesting a trimer-like structure. The inequivocal structural and stereochemical assignment for compound **4** was possible by single crystal X-ray diffraction,[11] and led to the assignment of the relative configuration of stereogenic centers present in the complexes. The complex consists of a trimer with crystallographic three-fold symmetry and contains three coordinated palladium atoms. The core of each molecule consists of a nine-membered ring of alternating Pd-S-CH atoms derived from β-ketosulfoxide ligand. The remaining two sites in each square-planar Pd coordination sphere are occupied by the oxygen of the carbonyl group and the *ortho*-carbon of the *p*-tolyl unit. The plane defined by the palladium atoms is sandwiched between two planes, one defined by the sulfur atoms and the other by the methyne carbon atoms.

The optical activity of the complexes has also been investigated. Complexes **4-6** exhibit a very high specific rotation $[\alpha]_D$= -486.5 (c= 0.2, $CHCl_3$) for **4**, $[\alpha]_D$= -375.5 (c= 0.098, $CHCl_3$) for **5** and $[\alpha]_D$= +130.3 (c= 0.112, $CHCl_3$) for **6**. Taking into account that the starting ligand was enantiomerically pure (with ***R*** configuration) and that a new stereogenic center has been formed during the reaction, we could expect the formation of two different diastereoisomers, depending on the stereoselectivity of the metallation. The study of the NMR spectra reveals the presence of only one set of signals corresponding to one diastereoisomer. Identical configuration at the two stereogenic centers could be established from the X-ray diffraction studies. Therefore, assumming that the configuration at sulfur atom is retained under the reaction conditions, we may assign the (***RR***) configuration to the complexes **4-6** (Fig 2).

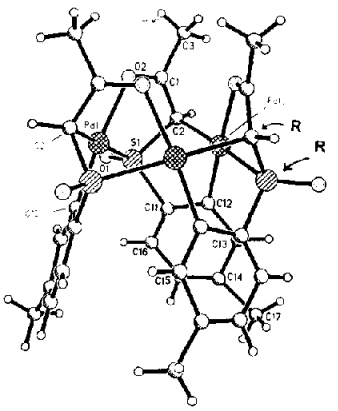
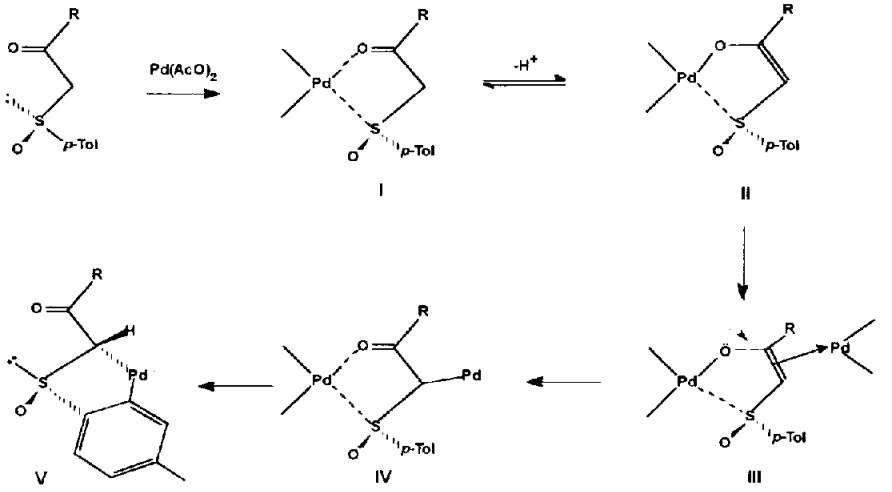


Figure 2

It seems evident that the formation of the palladacycle in complexes **4-6** must involve the initial formation of the Pd-C2 σ bond, because of the well known intramolecular character of the orthopalladation processes. On the other hand, the exclusive formation of the complex exhibiting the same configuration at

sulfur and C2 atoms, suggests that the formation of the Pd-C2 bond must be highly stereoselective. On this basis and taking into account the conditions used, we propose the following route to explain the formation of complexes. The first step might involve coordination of the lone pairs of the sulfur and carbonyl oxygen to $Pd(OAc)_2$, affording the species **I** (Scheme 2). The second step could, therefore, involve enolization of the carbonyl group, catalyzed by its previous coordination to palladium (both steps could take place simultaneously) to yield the intermediate **II**. This electron-rich olefin will immediately coordinate with Pd(II) yielding a π–olefin Pd(II) complex **III**, which is transformed to a σ-alkyl Pd(II), **IV**, by intramolecular electron donation from the enolic oxygen, restoring the carbonyl form. This species may evolve into the orthometallation product **V**, which must finally be transformed into the trimer.

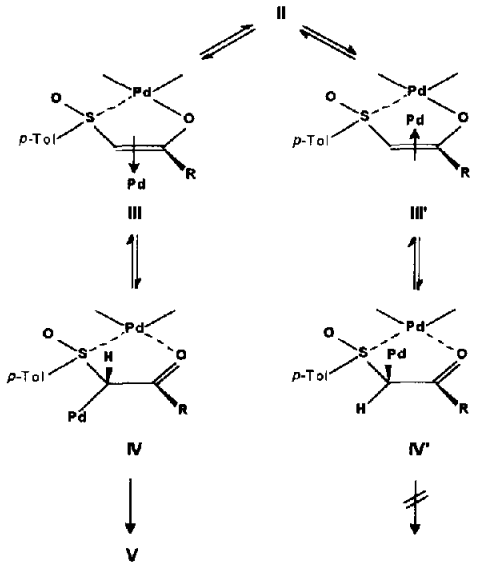


Scheme 2

The association of Pd(II) with the intermediate **II** could take place from either of the two sides of the double bond, resulting in two different π–olefin Pd(II) complexes, **III** and **III'**, which in turn evolve into two σ–alkyl Pd(II) complexes, **IV** and **IV'**, with different configuration at C2. However, the presence of an equilibrium between the intermediates **II**, **III** and **IV**, is possible, but the relative spatial arrangement of the Pd and the *p*-tolyl group in the complexes **IV** and **IV'** allows only **IV** to evolve into the orthometalated palladacycle. Hence, the equilibrium shift towards yields the diastereoisomer **V**.

Finally we must consider that the π–olefin Pd(II) and the σ–alkyl Pd(II) intermediates, **III** and **IV**, differ only in the possition of their respective electron pairs involved in the π bond as well as in the bonds with the two palladium atoms. Therefore, they are like two hyperconjugative forms of only one species, which would

exhibit averaged properties to those of the **III** and **IV**. In this case, the structure proposed for **V** (and therefore for the trimers **4-6**) could be also described as a resonance hybrid of two structures similar to those of **III** and **IV**. This description is compatible with the large $\Delta\nu$ observed for the C=O stretching in the IR spectra and with the relatively anomalous $\Delta\delta$ observed in the ^{13}C NMR spectra (see before). Nevertheless this assumption could not be supported from the X-ray data.



Scheme 3

In conclusion, we have reported the reaction of 2-*p*-tolylsulfinylethanones with palladium (II) acetate to form a new type of complexes composed by three molecules of ligand and three palladium atoms, where every ligand molecule is associated to two palladium atoms and vice versa. These complexes exhibit a stereogenic carbon directly joined to the metal. Their high enantiomeric purity (d.e.> 98%) indicates that the new stereogenic center was formed in a completely stereoselective reaction. The studies concerning the reactivity of these substrates, in order to achieve coupling reactions with chirality transfer are currently being investigated.

Experimental Section

The infrared spectra were recordered in Nujol mulls and KBr pellets in the 4000-200 cm^{-1} range with a Perkin Elmer Model 283 Spectrophotometer. NMR spectra were recordered on a Bruker WP-200-SY (200 MHz) spectrometer in $CDCl_3$ with TMS, as internal standard. The C, H and S analysis was carried out with a Perkin Elmer 240B microanalyzer.

All solvents were purified, prior to use, by the standard methods.[19] Palladium (II) acetate was purchased from Merck. The ligands were synthesized by published methods.[20]

Synthesis. A mixture of equimolar amounts of palladium (II) acetate with the corresponding ligand in glacial AcOH under N_2 was heated (*c.a.* 70°C) for 48-72 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. The combined extract was dried (Na_2SO_4), filtered and concentrated in vacuo. The crude residue was column chromatographed (SiO_2) eluenting with: AcOEt : Hex 1:9 yielding **4** (42%), AcOEt : Hex 1:8 yielding **5** (49%), Acetone : Hex 1:3 yielding **6** (50%).

Compound 4. $[\alpha]_D$= -486.5 (c= 0.2, $CHCl_3$). m. p. 348-350°C (decomposed). MS, m/z 901.6 (M^+ 14.2), 599.8 (1.94), 299.9 (2.86), 150.9 (98.6), 91.0 (100). Anal. Calcd C, 40.01; H, 3.33; S, 10.66. Found: C, 40.81; H, 3.76; S, 9.96. IR ν_{max} (cm^{-1}) 1556, 1114, 544, 584, 450.

Compound 5. $[\alpha]_D$= -375.5 (c= 0.098, $CHCl_3$). m.p. 350-352°C (decomposed). MS, m/z 943.8 (M^+ 1.02), 214.1 (100), 151.0 (31.6), 91.1 (61.2). Anal. Calcd C, 41.88; H, 3.95. Found: C, 41.20; H, 3.94. IR ν_{max} (cm^{-1}) 1570, 1127, 544, 584, 450.

Compound 6. $[\alpha]_D$= +130.3 (c= 0.112, $CHCl_3$). m. p. 293-294°C.Ms, m/z 1088.0 (M^+ 4.8), 151.0 (26.7), 105.0 (100), 91.0 (36.1), 77.0 (79.2). Anal. Calcd C, 49.67; H, 3.33. Found: C, 50.11; H, 3.75. IR ν_{max} (cm^{-1}) 1522, 1116, 578, 545, 493.

Acknowledgments

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